

1-1-2015

Aggregation in Complex Triacylglycerol Oils: Course Grained Models

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Introduction

Triacylglycerols (TAGs) are biologically important molecules found in the human body, and in many foods. They are the main structural element in some foods such as chocolate, butter, and cream. Because TAGs are efficiently stored by the human body in adipose tissue and are linked to maladies such as fatty liver disease¹, there is much interest in replacing TAG's in foods with other fat formulations that might provide health benefits. This makes the study of TAGs and the structures they form important to the food industry.

Many commercial fats consist of liquid oils trapped in a matrix of crystallized TAG structures. Transmission electron microscopy has shown that the unit crystal of these structures are isotropic crystalline nanoplatelets (CNPs). To understand TAG structures it is important to understand how CNPs spontaneously self-assemble under cooling.

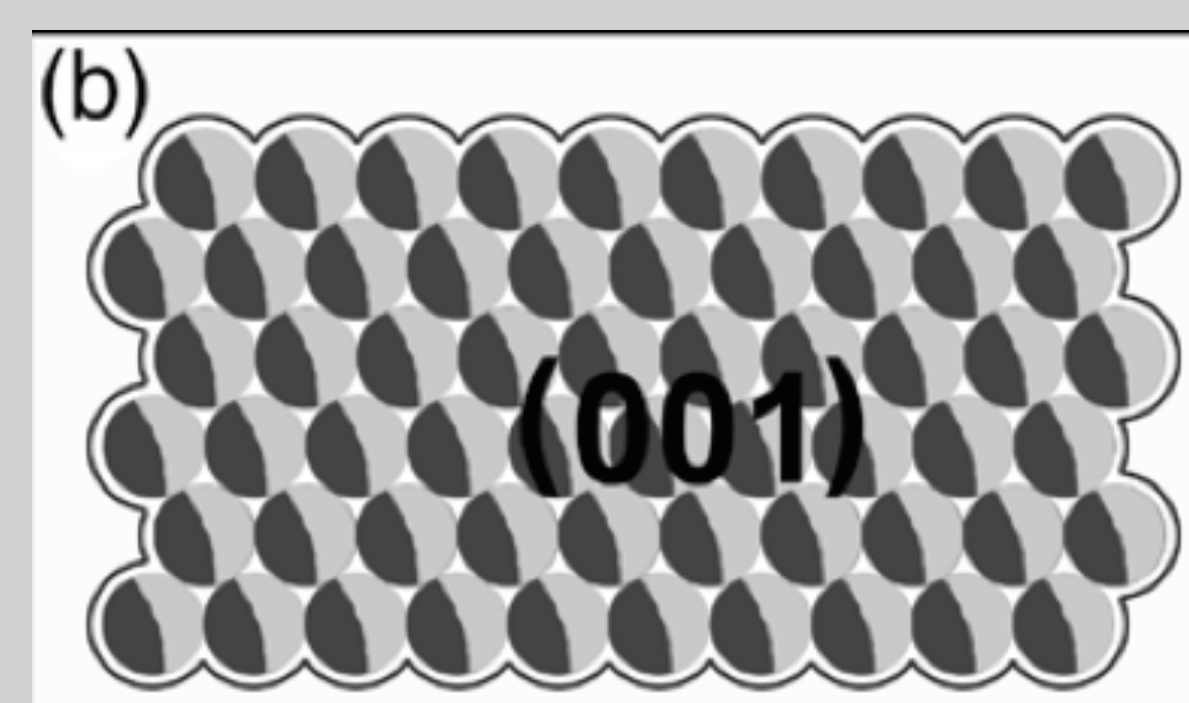
In this work we simulate a system consisting of solid CNPs as well as liquid TAGs which undergo phase separation on a nanoscale to coat the solid CNPs with an impenetrable layer. We then use the structure function to investigate the structures formed.

Methods

We model CNPs as rigid squares made up of a single layer of spheres (figure 1). The interaction between CNPs was modeled as a Van der Waals interaction which is felt between spheres belonging to different CNPs. The interaction has the following form for spheres of radius R a distance r from each other²:

$$V_d(R, r) = \frac{-A}{6} \left[2R^2 \left(\frac{1}{r^2 - 4R^2} + \frac{1}{r^2} \right) + \ln \left(\frac{r^2 - 4R^2}{r^2} \right) \right]$$

Figure 1: Model of a CNP

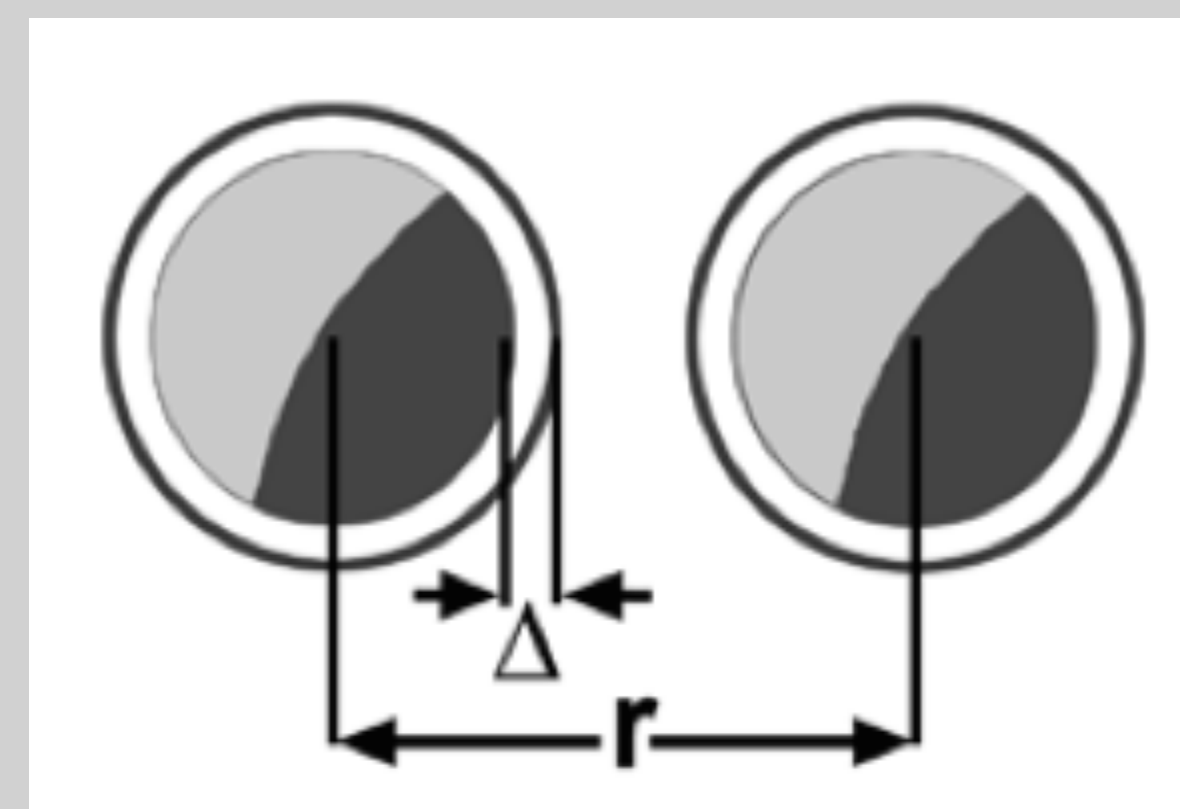


In our model electrostatic interactions were ignored.

The TAG coatings were modeled as an impenetrable layer of thickness Δ surrounding the spheres which make up the CNPs such the minimum possible distance between two component spheres of radius R is $2R + 2\Delta$ (Figure 2).

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Figure 2: Coating of thickness Δ on spherical components of a CNP



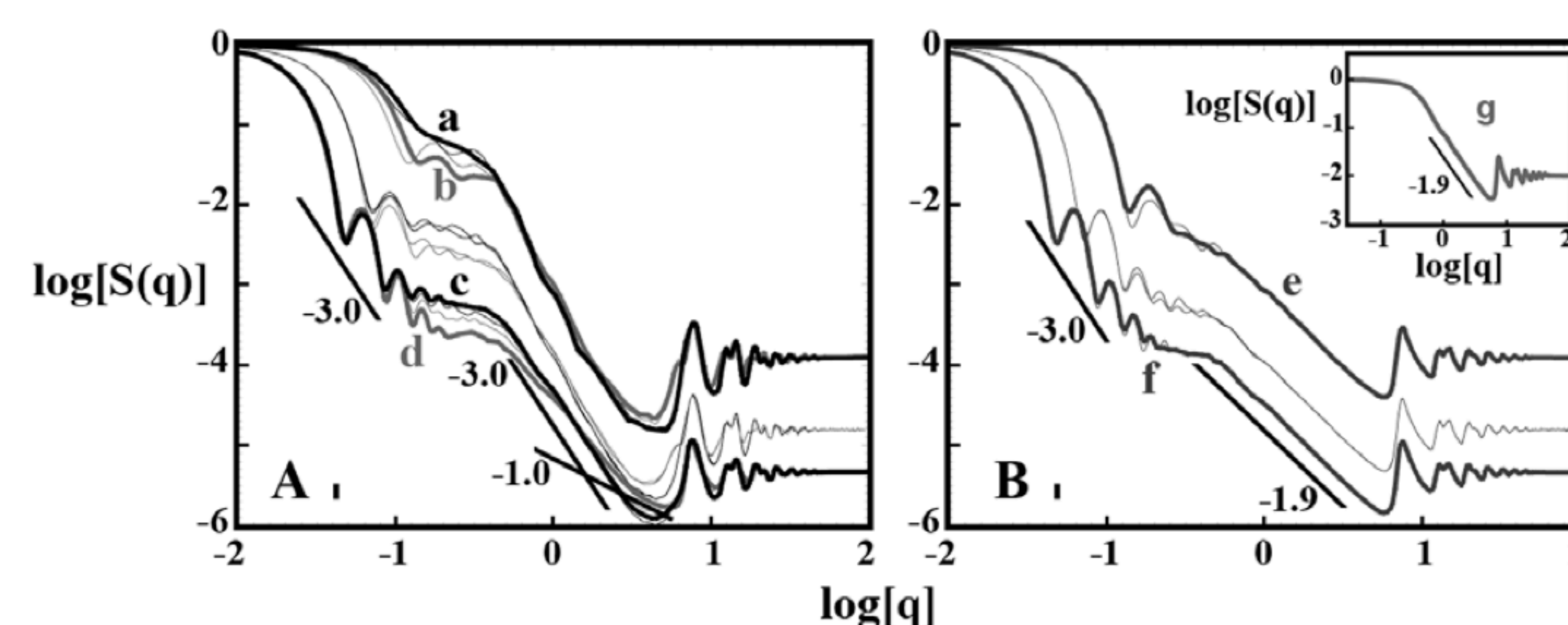
We use the Metropolis Monte Carlo algorithm to integrate the system. A single Monte Carlo step involves attempting translation and rotation of CNPs or clusters of CNPs, with moves that bring spheres inside $2R + 2\Delta$ of each other rejected. The simulation took place in a cubic simulation box with periodic boundary conditions. We simulated the system at a temperature of 300K for up to 10^6 Monte Carlo steps.

To analyze the resulting structures we used the structure function $s(q)$. It can be shown that if the system has a fractal structure $s(q) \sim q^{-D}$ where D is the fractal dimension of the system³. This allows us to make inferences about the structure of the system on different scales.

Results

We chose values of Δ between 0.0124u and 0.2906u where u is an arbitrary unit used within the simulation.

We identified we identified three regimes in this range, a thin regime, transition regime, and thick regime. We chose the following values of Δ characteristic of each regime: $\Delta = 0.0124$ u (thin region), $\Delta = 0.0701$ u (transition region) and $\Delta = 0.1124$ u (thick region). See figure 3 for a plot of the logarithm of the structure function as a function of $\log(q)$.



We found that:

1. Each of the three regimes can be identified based by the structure function.
2. A thin coating ($\Delta < 0.0701u$) allows the formation of 1D "TAGwoods" which consist of stacks of CNPs arranged face to face, held together by their mutual attraction. These could then aggregate to form diffusion limited and reaction limited aggregation clusters, though this was not observed in this work due to constraints on simulation time. These clusters should then be randomly distributed in space.
3. In the transition regime ($0.0701u < \Delta < 0.0916u$) the TAGwoods are only weakly bound to each other and aggregates of TAGwoods are no longer stable structures. TAGwoods remain randomly distributed in space.
4. In the thick coating regime ($\Delta > 0.0916$) TAGwoods themselves are no longer able to form and CNPs remain randomly distributed in space.
5. By equating 1u to 100nm, we are able to predict the concentrations of liquid TAGs which will yield coatings in each region. These are 0.29% for thin coatings, 0.67% for coatings in the transition regime, and 0.94% for thick coatings.

Hamaker Interaction

The interaction potential V_d between two spherical components of the CNPs that we modeled is derived by considering the spheres as being made up of point particles, each with an attractive potential given by $V_d = -1/r^6$. The interaction between the two spheres as a whole is calculated by integrating this potential over the first sphere to find the interaction between the first sphere and a single point on the second, then integrating this over the second sphere to find the total interaction. This was first done by H.C. Hamaker⁴.

One can perform a similar calculation for a general potential of the form $V_d = -C_n / r^n$. For $n > 7$ we find the following formula:

$$V_n(R_1, R_2, r) = \frac{4\pi^2}{r} \frac{\rho_1 \rho_2 C_n}{(n-2) \dots (n-7)} \left(1 - R_1 \frac{d}{dR_1} \right) \left(1 - R_2 \frac{d}{dR_2} \right) \otimes \left[\frac{1}{(r + R_1 + R_2)^{n-7}} - \frac{1}{(r - R_1 + R_2)^{n-7}} - \frac{1}{(r + R_1 - R_2)^{n-7}} + \frac{1}{(r - R_1 - R_2)^{n-7}} \right]$$

In this equation R_1 and R_2 are the radii of spheres 1 and 2, and r is the center to center distance between the spheres.

For sufficiently large spherical particles at close distances, we can obtain a simpler expression for the potential between the two spheres of radius R using the Derjaguin approximation. We treat the two spheres as though they are made up of a series of progressively larger cylindrical shells nested within each other. To find this interaction we begin with an expression for the potential between two walls of infinite depth and area A a distance l apart:

$$V_{ww} = \frac{2\pi \rho_1 \rho_2 C_n A}{(n-2)(n-3)(n-4)l^{n-4}}$$

Noting that the potential between point particles drops off as the sixth power of distance, we make the assumption that we only need to consider the wall-wall interaction between the two closest cylindrical shells. The interaction between a pair of shells is then found to be:

$$V_{shell} = \frac{2\pi \rho_1 \rho_2 C_n}{(n-2)(n-3)(n-4)(l + R\theta^2)^{n-4}} 2\pi R^2 \theta d\theta$$

Where l is now the minimum distance between the surfaces of the spheres. To find the full interaction between the spheres we integrate over all angles from 0 to infinity, knowing that the contribution from large angles will be negligible. Completing this integral, we find the Derjaguin approximation for the interaction between spheres to be:

$$V_{der}(r) = \frac{AR}{(r - 2R)^{n-5}} \quad \text{where} \quad A = \frac{2\pi^2 \rho_1 \rho_2 C_n}{(n-2)(n-3)(n-4)(n-5)}$$

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada, by the Advanced Food and Materials Network of Centres of Excellence (AFMnet), by the Atlantic Computational Excellence Network (ACEnet) and by the U.S. NSF under Grant No. DMR-0906618.

References

1. Adams L A, Lymp J F, St Sauver J, Sanderson S O, Lindor K D, Feldstein A and Angulo P 2005 *Gastroenterology* **129** 113–21
2. Hamaker H C 1937 *Physica* **4** 1058
3. Viscek T 1999 *Fractal Growth Phenomena* 2nd edn (Singapore: World Scientific)

Figure 3. Structure function, for different thicknesses of nano-phase separated layers of oil on the surfaces of CNPs, and different simulation volumes. , $L = 100$ (unlabeled central set), $L = 150$ (c, d, f). **A**: $\Delta = 0.0124$ u (a, c), $\Delta = 0.0701$ u (b, d). **B**: . Insert (g) shows $S(q)$ for a single CNP. The maximum error bars are shown next to the lettering **A** and **B**.